The Development of Organic Conductors, Including Semiconductors, Metals and Superconductors

Lessons from History
Organic Electronic *(MOLECULAR)* Materials

- Design
- Ensemble
- Properties
Organic Conductors, Early History
Charge Carrier Generation: Electron Donors


Photogeneration

Per(I$_2$)$_3$ $\sigma_{RT} = 0.5$ S/cm


Per(I$_2$)$_4$ $\sigma_{RT} = 30 - 50$ S/cm (metal to ca 270K)


Perylene (Per)

facile oxidation
Proposed Structure of Perylene Iodides

(a) PERYLENE · 1.5 I₂  (b) PERYLENE · 3 I₂
Charge Generation: Electron Acceptors, Acceptor Repertoire

Quinone

Chloranil

TCNQ

facile reduction

Types of C-T Complexes

Simple

\( D_{(1)}T_{(1)} \)

\( \sigma_{RT} = 10^{-12} - 10^{-6} \)

e.g. \( \text{Li TCNQ} \)

Complex

\( D_{nTm} \)

\( \sigma_{RT} = 10 - 100 \)

e.g. \( Q \text{ TCNQ}_2 \)

\( Q = \) \[
\begin{array}{c}
\text{N} \\
\text{CH}_3
\end{array}
\]
## Conductivities of Simple and Complex TCNQ Salts

<table>
<thead>
<tr>
<th>Cation</th>
<th>Simple</th>
<th>Complex</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Simple Cation" /></td>
<td>$10^{-8}$</td>
<td>$\approx 10^2$</td>
</tr>
<tr>
<td><img src="image2" alt="Complex Cation" /></td>
<td>$10^{-14}$</td>
<td>$\approx 10^{-1}$</td>
</tr>
<tr>
<td><img src="image3" alt="Complex Cation" /></td>
<td>$10^2$</td>
<td>$\approx 10^{-1}$</td>
</tr>
</tbody>
</table>
The Birth of TTF

An Important Design Feature

\[(\text{4n} + 2) \pi \text{ electrons}\]
The Marriage of TTF & TCNQ

e^(-) + e^(-) E_{1/2} = 0.37 vs SCE

E_{1/2} = 0.22 vs SCE
TTF-TCNQ, The First Organic Metal

The “Giant Conductivity Peak” Phenomenon


**FIG. 3.** Temperature dependence of the conductivity of (TTF) (TCNQ) single crystal (---●---●---) and of (TTF) (TCNQ) typical crystals (---○---○---).
Two Possibilities of Flat Molecule Ensembles

Alternating Stack

Segregated Stack
The Structure of TTF-TCNQ
A Problem with Transport in a ½ Filled Stack (Band)

Strong Coulomb Repulsion
Soos-Torrance Model
(Mixed Valence)

"No" Coulomb Repulsion
Facile Conductivity in Complex Salts of TCNQ
Synthesis of TTF and Derivatives

Strategy

\[
\text{Structure 1} \quad \equiv \quad 2 \times \text{Structure 2} \quad \equiv \quad \text{Structure 3}
\]
Synthesis of 1,3-Dithiole-2-thiones

Schukat, G.; Richter, A.M.; Fanghänel, *Sulfur Reports*, 1987, 7, 155 - 240
Synthesis of TTFs

Schukat, G.; Richter, A.M.; Fanghänel, Sulfur Reports, 1987, 7, 155 - 240
The Most Popular and Unusual Tetrachalcogen Fulvalenes

\[ \text{S, Se} = \text{Superconducting}; \quad \square = \text{not yet prepared} \]
The Most Popular Acceptors

Metal Dithiolenes

mnt
dmit
TTF-TCNQ, The First Organic Metal

Why the loss in conductivity?
Dealing with the Peierls Catastrophe: Increase in Dimensionality and Disorder

HMTSF-TCNQ

Comparative Temperature-Dependent Resistivities

The DCNQI Story: A Truly 3-D Molecular Metal

Hünig, S. J. Mat. Sci. 1995, 5, 1469 - 1480
Temperature Dependence of the Conductivity Of the Copper Complexes
Copper-Mediated 3-Dimensionality
View of a Single Layer
A Molecular Metal Designer’s Dream: The Single Component Metal

The Key Building Block

\[
\text{dmit}
\]

Metal Dithiolenes
Temperature Dependence of the Resistivity & Magnetic Susceptibility

Hisashi Tanaka,1 Yoshinori Okano,1 Hayao Kobayashi, Wakako Suzuki, Akiko Kobayashi*
Another Single-Component Conductor

Take Home Messages from this Lesson

1. Facile oxidation = $p$-doping

   Perylene (Per)

   Facile reduction = $n$-doping

   TCNQ
Take Home Messages from this Lesson

2.

Need charge AND unpaired Spin to observe high conductivity
Summary

Organic materials based on molecular solids, while showing conductivities as high as those of some traditional metals, also exhibit other very unusual properties.

The lessons learned from organic metals apply directly to conducting polymers.
The End

Thanks!
Discussion
Coffee!
The “Giant Conductivity Peak” Phenomenon

1973, 12, 1125 - 1132

**FIG. 3.** Temperature dependence of the conductivity of (TTF) (TCNQ) single crystal (— ● — ● —) and of (TTF) (TCNQ) typical crystals (— ○ — ○ —).
The Measurement of Conductivity

\[ R = \frac{V}{i} \]

\[ R = \frac{\rho l}{s} \]

[\[ \sigma = \frac{1}{R} \]

\[ R = \text{resistance}, \ V = \text{Potential difference}, \]
\[ i = \text{current}, \ \rho = \text{resistivity}, \ \sigma = \text{conductivity}, \]
\[ s = \text{cross sectional area} \]
\[ \sigma_{ii} \sim 10^3 \sigma_{ii} \]
\[ \frac{\sigma_{ii}}{\sigma_{ii}} = f(T) \]